

GEOCHEMICAL AND MINERALOGICAL COMPOSITION OF SEDIMENTS CORED FROM THE ANOXIC ZONE OF THE WESTERN BLACK SEA BASIN

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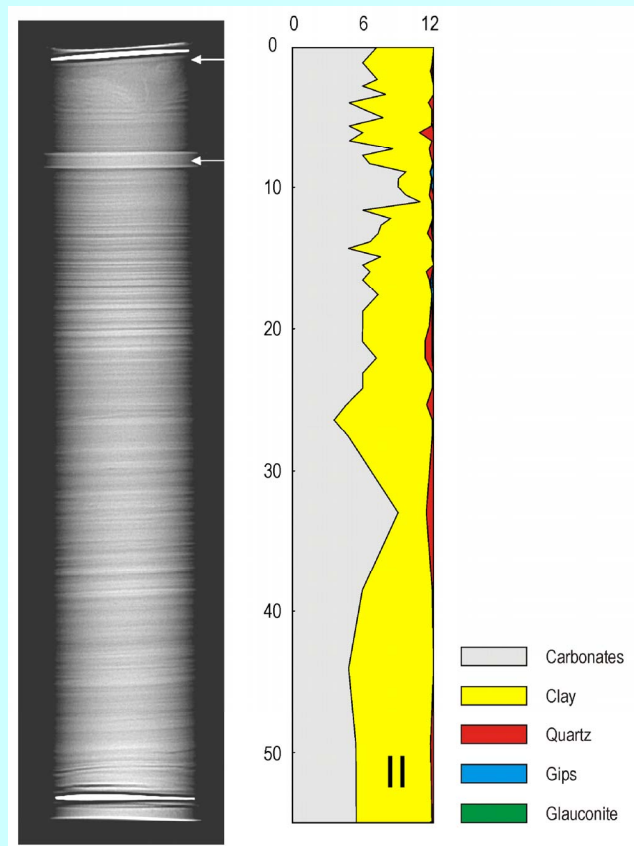
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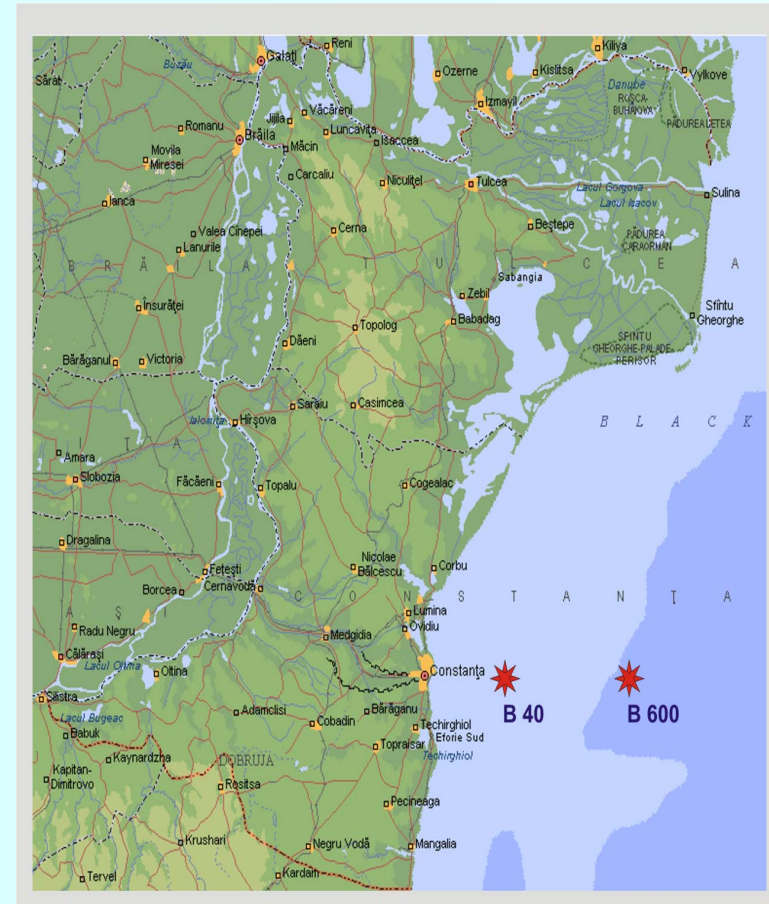
C.I.CRISTACHE et al,
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Samples



Digital radiographic image of the BS – 600 core (left) together with a graphic representation of main lithologic components (right).



Aim

- Provide new data concerning any relationship between investigated elements for a better understanding of the past evolution of the anoxic zone of the Black Sea.

Materials and methods

- ❑ Gamma ray spectrometry (^{137}Cs & ^{210}Pb)
- ❑ NAA (ENAA & PGAA)
- ❑ Principal components analysis

Samples

- The core was sliced into 45 fragments, with thickness gradually increasing from 5 mm at the surface to 40 mm at the bottom.
- Each segment was then dehydrated at 105°C, homogenized and divided in four aliquots, two of about 1 to 3 g for ENAA and PGAA, one of 15 to 100 g for radiometric assay and finally one of about 10 g for additional mineralogical investigations.

Irradiation

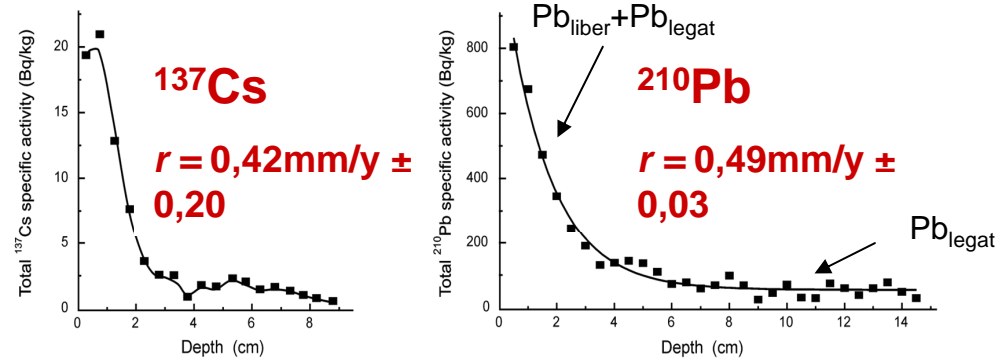
- Epithermal Neutrons Activation Analysis (ENAA) was performed at the Joint Institute of Nuclear Research (JINR), Dubna (Russia) at IBR-2 reactor, by using all energy spectra of neutrons at an average fluency debit of about $5 \cdot 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$.
- Prompt Gamma Neutron Activation Analysis (PGAA) was performed at the BNC Research Reactor (Budapest,) by using all energy spectra of neutrons at an average fluency debit of about $1,5 \cdot 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$

Statistical assessment

- To evidence any similarities or dissimilarities between investigated as well as model rocks (UCC, MORBs) we have used Principal Component Analysis (PCA) as well as Correlation analysis (CA) in R-mode, two techniques of analysis of multivariate data.
- R-mode implies that each sample representing a case is described by means of corresponding content of major components, trace elements or REE representing variables.

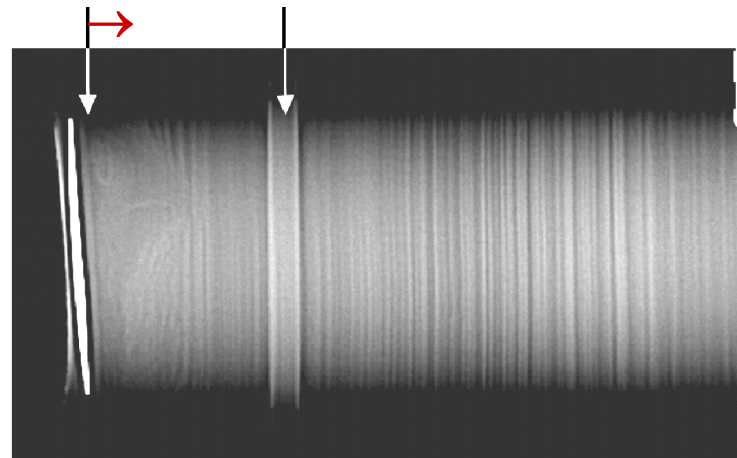
Results

Gama spectro-
metry was used in
order to obtain
the vertical
profile of ^{137}Cs
(Chernobyl) and
 ^{210}Pb
specific activity



In this way, we
came to the
conclusion that
the core can be
regarded as an
environmental
archive for the
last millennium.

← 1000 – 1200 years



Analyses elements :

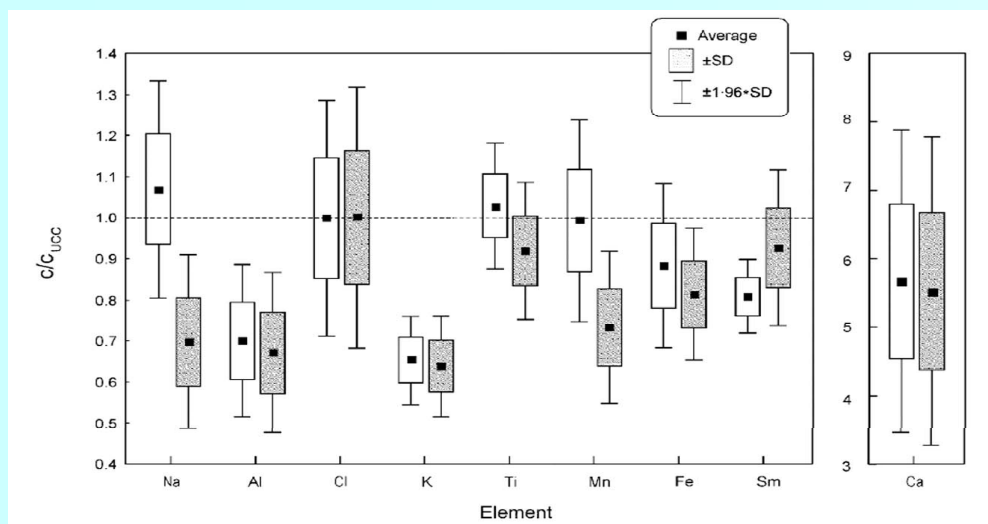
8 (rocks forming elements)

Na, Al, Si, Cl, K, Ca, Ti, Fe

34 (trace elements)

1 H	B, Sc, V, Cr, Mn, Co, Yn, As, Se, Br, Rb, Sr, Y, Zr, Mo, Sn, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Dy, Yb, Hf, Ta, W, Th și U																2 He	
3 Li	4 Be																	10 Ne
11 Na	12 Mg																	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	89 Ac	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Me	102 No	103 Lw		

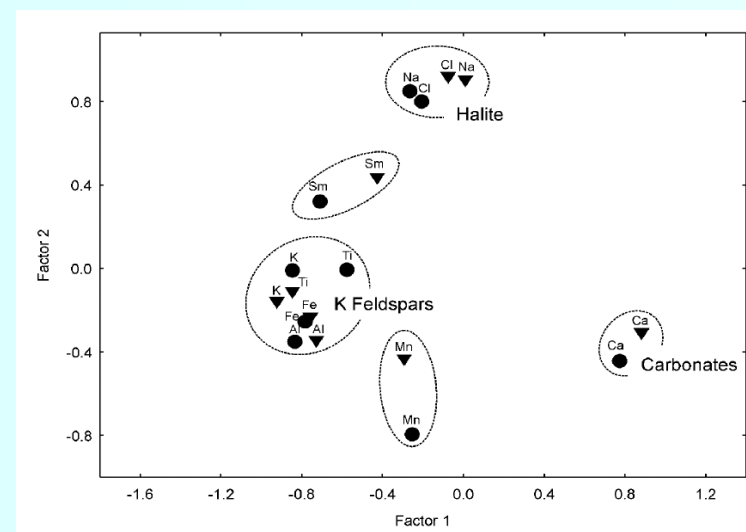
An ENAA and PGAA comparative study



Box and whiskers diagram of the average concentrations of investigated elements relative to UCC concentrations (white - PGAA, gray - ENAA).

From all investigated elements, except Na and Mn, the concentrations of all other elements involved in this intercomparison were coincident within one standard deviation which attests the accuracy of this test.

At the same time, the Ca concentration was about six times greater than that of UCC, this significant enrichment being due to the presence of considerable deposits of shell debris in the neighbourly oxygenated zone, a characteristic of the Western Black Sea Continental Platform.

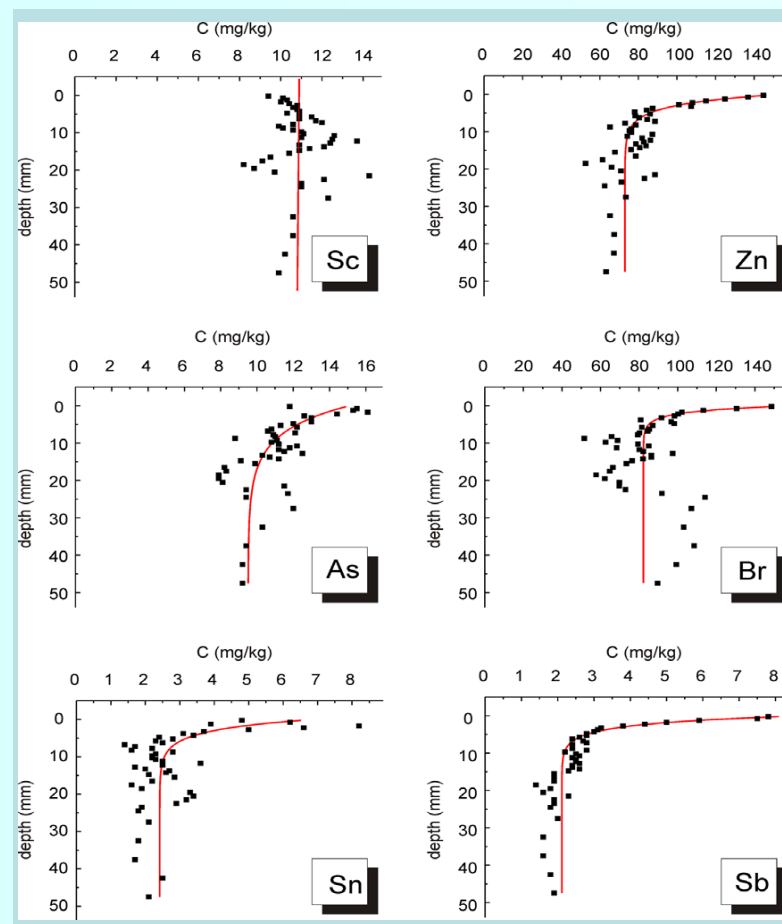


PCA plot of the components of investigated sediments; ● PGAA, □ ENAA.

The presence of five clusters, consisting of equal number of points corresponding to both methods attest the compatibility of methods as well as of laboratories, while at least three clusters could be ascribed to three mineralogical components of sediments, i.e., halite, feldspars and carbonates.

All these elements presented increasing concentrations towards the upper limit of sediments, which were greater than alert concentrations in the cases of As and Br, as in accordance with Romanian Environment Regulations.

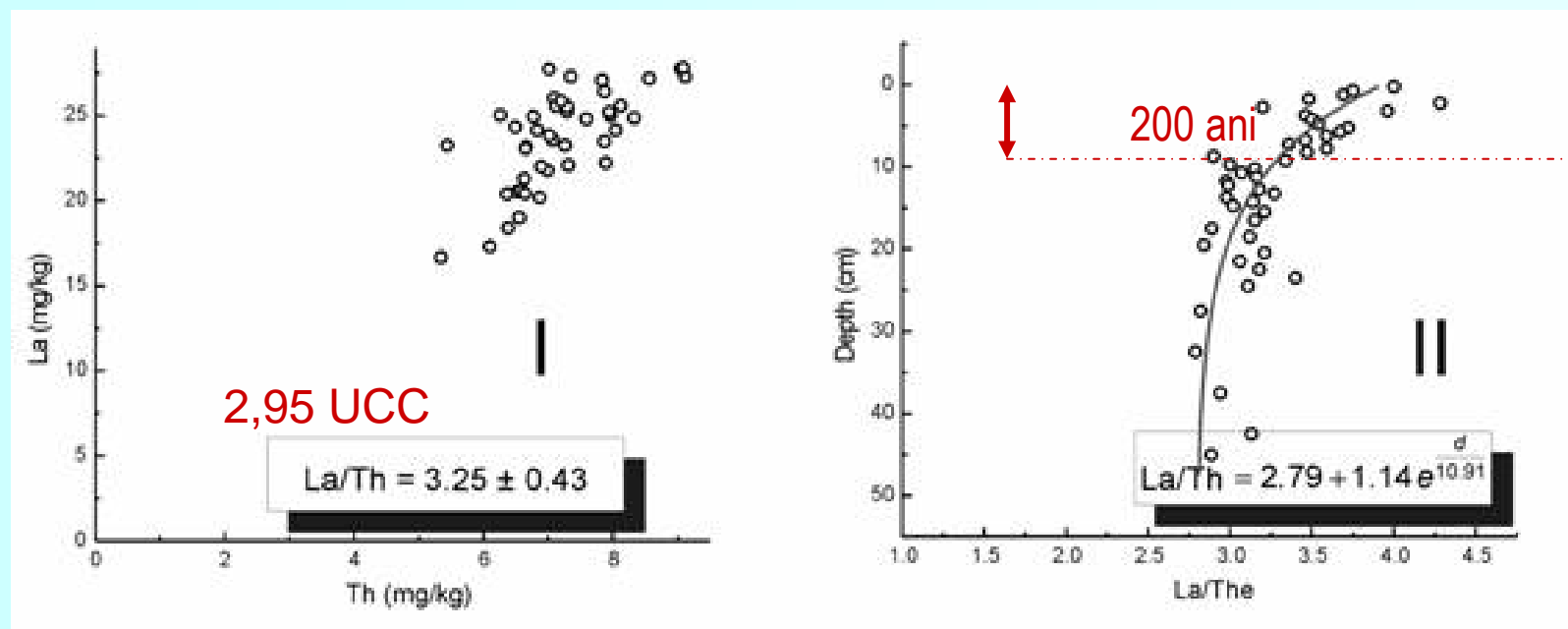
The region could be characterized by increasing elemental concentrations that correspond to the last 100 years, i.e., the industrialization period in Europe, by utilizing Chernobyl ^{137}Cs as a time marker.



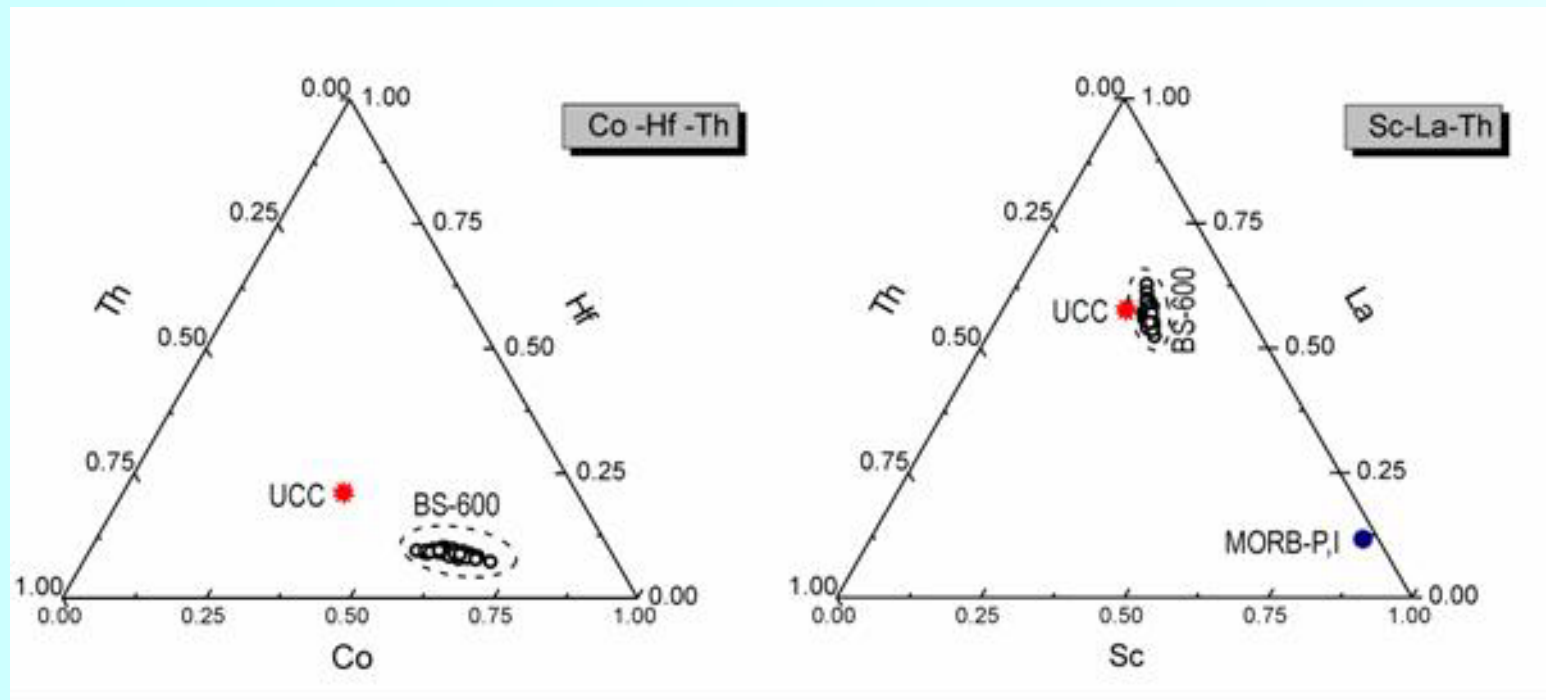
Vertical distribution of Zn, As, Br, Sn, and Sb as presumed pollutants and Sc, which is considered a natural element.

NAA

- In our case we have noticed an average value of La/Th is 3.25 ± 0.43 , consistent with UCC, but a more careful observation of the vertical distribution of this ratio along sediment column, we have noticed that this ratio is almost constant between 20 and 50 cm and equal 3.1 ± 0.14 , but monotonously increases to the sediments surface to almost 4. This behavior in some way confirms the fact that in the last 300 ± 60 years the mineral composition of sediments varied.



Sediments origin

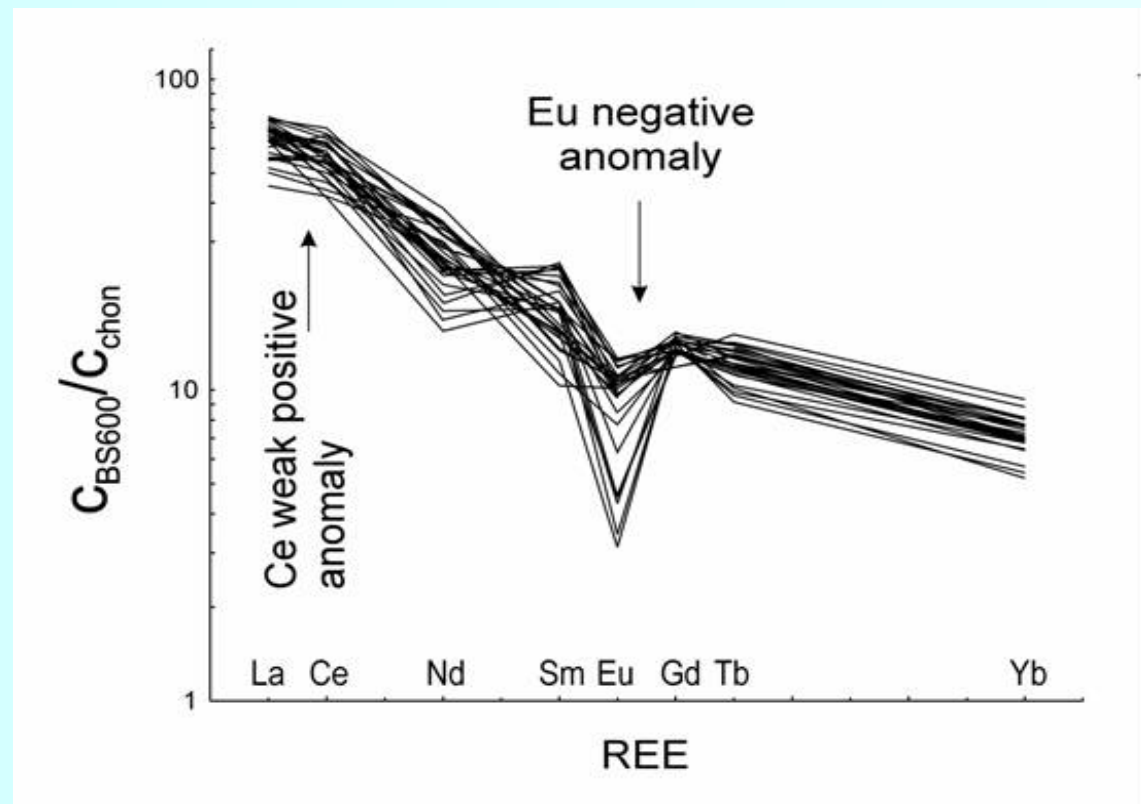


La-Sc-Th and Co-Hf-Th ternary diagrams illustrating the BS-600 sediment composition with respect to UCC and MORBs (Pacific and Indian Oceans). On both diagrams the sediments points are in the close vicinity of UCC.

NAA

Sediments origin

A chondrite normalized plot of 9 Rare Earth Elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy and Yb) showed the presence of a weak Ce positive anomaly, explained by the existing anoxic environment as well as significant Eu negative anomaly, confirming the association of heavy metals with the terrigenous, continental fraction of sedimentary material.



List of publish paper

- **Cristache, C.I.**, Gmeling, K., Culicov, O.A., Toma, M., Dului, O.G. (2009). An ENAA and PGAA comparative study of anoxic Black Sea sediments, Journal of Radioanalitical and Nuclear. Chemistry 67, 939-943.
- Dului, O.G., **Cristache, C I.**, Oaie, G., Culicov, O.A., Frontasyeva ,M.V., Toma, M., (2009). ENAA Studies of Anoxic Black Sea Sediments, Pollution Marine Pollution Buletin, 58, 827-831.
- Dului O.G., **Cristache C.I**, Oaie G., Ricman C, Culicov O.A, Frontasyeva M.V, (2010), Epithermal Neutron Activation Analysis of Some Geological Samples of Different Origin, 7th International Conference of the Balkan Physical Union, Alexandroupolis, AIP Conf. Proc., 1203, 489-494.
- Dului, O.G., **Cristache C.**, Oaie G., Culicov O.A., Frontasyeva M.V, Toma M. (2009) On the distribution of major and trace elements as determined by epithermal neutron activation analysis in unconsolidated sediments of the anoxic continental platform of the Black Sea, Book of Abstracts, ISINN-17, 27-30 May , Dubna, p. 25.
- Dului, O.G., **Cristache, C.I.**, Oaie, G., Culicov, O.A, Frontasyeva M.V. (2009). Cs-137 geochronology, epithermal neutron activation analysis, and principal component analysis of heavy metals pollution of the Black Sea anoxic continental shelf sediments Geophysical Research Abstracts, Vol. 11, EGU2009-4992,Vienna.
- Dului, O.G., Culicov O.A., **Olteanu, C.I.**, Ricman C., Mihailescu N.,Frontasyeva, M.V., Dinescu, L., Oaie, G., (2008). Instrumental neutron activation analysis applications to environmental and geological studies, Book of Abstracts, ISINN-16, Dubna.

Concluding/Remarks

- ❑ Taking in consideration the anoxic character of investigated sediments, that represents a good archive for past evolution of Black Sea
- ❑ NAA because it enables to determine the concentrations of major elements (rock forming elements) as well as trace elements, allowed the extraction of such information, while the absolute geochronology carried out using ^{137}Cs and ^{210}Pb is essential in development of past evolution of Black Sea
- ❑ PCA represents a precious auxiliary

Acknowledgement

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Many thanks for your attention!

